



PERGAMON

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FABRICATION AND CHARACTERIZATION OF A BIOACTIVE GLASS COATING ON TITANIUM IMPLANT ALLOYS

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Abstract—Ongoing research is reported aimed at improving biofixation through the use of bioactive glass coatings on Ti-based implant alloys. The optimized processing conditions for coating with one promising bioactive glass composition are discussed, and the stress corrosion crack growth behavior in a simulated human physiological environment is presented. This glass can be successfully used to coat Ti implant alloys, and preliminary tests indicate that interfacial fracture resistance is good. © 1999 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Biomaterials; Titanium alloys; Non-metallic (silicates); Bonding; Stress corrosion

1. INTRODUCTION

Bioactive glasses are special glasses that, due to their composition, will undergo a series of chemical reactions, reviewed in Ref. [1], in the presence of the human physiological environment and form hydroxycarbonate apatite (HCA) on their surfaces. HCA is sufficiently similar to biological apatites that the body effectively recognizes the modified surface as bone-like and will deposit bone tissue on it; in fact, some bioactive glasses will also form bonds with soft collagen-based tissues as well [1]. This bioactive nature, combined with the relative ease in which glasses can be processed, suggests that these glasses could be used as coatings on biological implants that would allow stable mechanical fixation to bone. One barrier to using these glasses as implant coatings is the high thermal expansion coefficients of the original bioglass compositions, about $14\text{--}15 \times 10^{-6}/^{\circ}\text{C}$ [2], relative to those of Ti-alloys (the most widely used long-term implant metals) which have thermal expansions of $9\text{--}10 \times 10^{-6}/^{\circ}\text{C}$. As a result, the typical bioactive glass compositions (e.g. Bioglass[®] 45S5 [3]) cannot be used for such coating applications because the glass cracks due the thermal stresses invoked during the heating/cooling cycle used to apply the glass films.

A promising bioactive glass composition, designated 6P57 (Table 1), has emerged from a new series of bioactive glasses developed in the family Na–K–Ca–Mg–P–Si–oxide and has been applied to Ti–6Al–4V while maintaining good mechanical

integrity [4]. This glass has proven to be bioactive [4] with an essentially uniform HCA layer forming after one month (Fig. 1) in a simulated body fluid (SBF) [5]. The processing conditions over which good coatings can be obtained has been defined [6] and will be briefly reviewed in Section 3. Despite this success, the subcritical crack growth behavior of this glass and its interface with the Ti-alloy must be well characterized to assure long-term mechanical stability of the implant in the body. This work has begun and will be discussed in Section 3.

2. EXPERIMENTAL PROCEDURE

The glasses are prepared by mixing 99.9% silica powder and reagent grade NaPO_3 , Na_2CO_3 , K_2CO_3 , CaCO_3 , and MgO in the appropriate proportions to obtain the final glass composition. The starting powders were suspended in either isopropyl or ethyl alcohol and mixed using a high speed stirrer. After drying, the mixtures were melted in a Pt crucible in air at 1400°C for 4 h and cast in a graphite mold to make $10 \times 40 \times 50 \text{ mm}^3$ plates. The plates were then ground into powders by planetary ball milling with agate balls, and slurries were prepared in isopropyl alcohol. Green coatings were applied to Ti–6Al–4V substrates via sedimentation from the prepared slurries and then fired using a Unitek dental furnace. The general firing schedule was to preheat the furnace to 600°C in air followed by a simultaneous rough evacuation (to $1.3 \times 10^4 \text{ Pa}$) and thermal ramp ($40^{\circ}\text{C}/\text{min}$) to the desired soak temperature ($700\text{--}820^{\circ}\text{C}$). After 30 s at the soak temperature, furnace vacuum was released,

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Table 1. Glass compositions in wt%

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	P ₂ O ₅	Al ₂ O ₃
6P57	56.5	11	3	15	8.5	6	
Bioglass [®]	45	24.5		24.5		6	
Soda-lime	72	14	1	7	4		2

and the specimens were lowered from the furnace to cool to room temperature.

The stress corrosion crack growth (SCCG) properties of the 6P57 bioactive glass were measured using double cantilever beams (DCBs) [7] having dimensions of width, $B=5$ mm, height, $2h=8$ mm, and length, $L=50$ mm. Beams were side grooved ($300\text{ }\mu\text{m}$ wide) along the length of the beam centerline leaving a web approximately one-third the thickness of the beam to enforce crack growth along the beam centerline. All specimens were pre-cracked in air and then tested in flowing SBF (~ 0.5 l/min) at 37°C using a fixed applied load that consisted of weights on a graphite hanger suspended from the loading tabs on the specimen. Crack lengths were monitored using both direct optical measurement and crack mouth opening compliance. Crack mouth opening was monitored using an induction based displacement gage manufactured by Kaman Instruments, and specimen compliance was used to determine crack lengths based on the following equation:

$$\frac{EBv}{P} = f\left(\frac{a}{h}\right) \quad (1)$$

where E is the elastic modulus of the glass, B the beam width, v the mouth opening displacement, P the load, and $f(a/h)$ the calibration function relating crack length, a , and beam half height, h , to the compliance of the specimen. The calibration function was determined by making a polynomial fit of measured crack lengths (obtained optically) and the corresponding specimen compliances taken from a glass DCB sample of similar dimension to those used for the SCCG measurements.

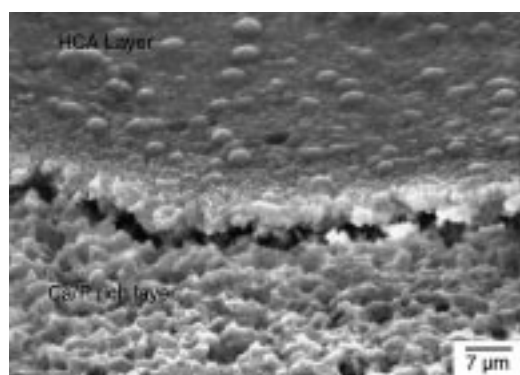


Fig. 1. HCA formation on 6P57 bioactive glass after one month in SBF.

3. RESULTS AND DISCUSSION

As noted in Section 1, crack free coatings of the bioactive glass 6P57 showing good mechanical adherence have been deposited on Ti-6Al-4V alloy. The processing parameters that will give acceptable coatings were bounded by performing a series of coating experiments at differing time and temperature cycles (Fig. 2). The interface chemistry was evaluated by wavelength dispersive and calibrated energy dispersive spectroscopic analyses, and it was found for the most adherent coatings that there was not a resolvable reaction layer between the glass and the Ti-6Al-4V substrate [4, 6]. However, transmission electron microscopy performed by Oku *et al.* [8] has revealed a relatively continuous 50–100 nm thick layer of Ti_5Si_3 . Thus, it is believed that the bonding mechanism of glass coating to the Ti-6Al-4V substrate is as follows [6]:

1. dissolution of the native titanium oxide on the substrate by the glass at the firing temperature;
2. the glass then wets the clean Ti-alloy surface;
3. the Ti_5Si_3 forms between the glass and Ti-alloy substrate;
4. to obtain optimal adhesion, the firing time and temperature should be strictly controlled to attain a thin silicide layer and avoid bubble formation at the interface as a result of overreaction.

Preliminary tests of the coating adherence have been performed using a series of indentations both

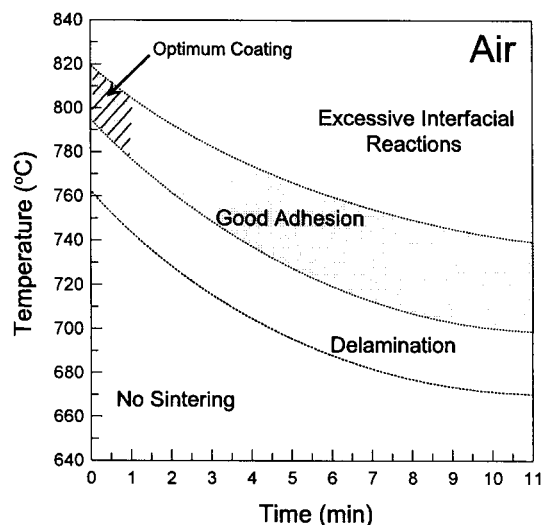


Fig. 2. Processing map for bioactive glass 6P57 in air [6].

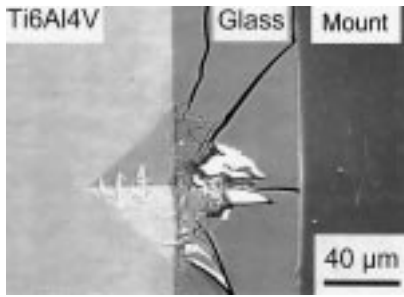


Fig. 3. Indentation of 6P57/Ti-6Al-4V interface.

on the coating surface and at the glass/metal interface on polished cross-sections [4, 6]. It has been found that indentations on the coating surface that penetrate through to the interface do not cause debonding of the coating from the Ti-alloy substrate. When indentation loads were above approximately 500 g there was significant spalling around the indent, yet the spall cracks did not propagate along the interface. Instead, they propagated in the glass just above the interface leaving a thin adherent layer of glass remaining on the Ti-6Al-4V substrate. This behavior was supported by indentations placed directly on the interface of sectioned samples. Invariably the cracks would propagate out into the glass and not along the interface (Fig. 3). Although these tests are not quantitative measures of the glass/Ti-alloy interface toughness, they provide clear qualitative support that the interface has a sufficient toughness to force the crack into the bulk bioactive glass. Quantitative interface toughness testing in SBF is currently underway and will be presented in a future publication.

As this new bioactive glass is expected to be used as a fixation aid for biological implants, it will be subject to various loading conditions that reflect the implant location within the body. Because of the corrosive nature of biological fluids and the fact that silicate glasses are known to experience subcritical crack growth in aqueous environments [9–12], special attention must be given to evaluating the SCCG resistance of the glass and the glass/Ti-alloy interface. Indentations performed in SBF gave similar results to those in Fig. 3; thus, the stress corrosion crack growth behavior of the bulk bioactive glass may be the controlling factor.

It was found (Fig. 4) that the 6P57 had similar SCCG properties to the original Bioglass® 45S5 composition [13], and both glasses were similar to the published “parent” soda-lime glass SCCG behavior [14]. Note that the soda-lime glass data were taken in water at 25°C and not in SBF at 37°C. It would appear from these data that SCCG in these glasses is not dramatically influenced by their varying composition (Table 1). For crack velocities about 10^{-2} – 10^{-3} m/s, viscous drag may inhibit crack extension [15]. At lower velocities, it may be contemplated that the reactivity of the bioactive

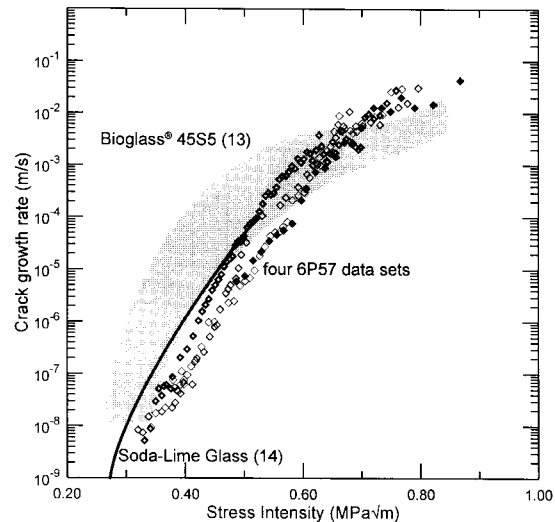


Fig. 4. Four SCCG curves of 6P57 (data points) tested in SBF at 37°C. Soda-lime glass is shown as a line. Bioglass® 45S5 is shown as a gray scatter band.

glasses with the SBF could cause the following behaviors:

1. HCA could grow on the crack flanks and “heal” the crack at low crack velocities, or at least inhibit fluid access to the tip;
2. stress-driven dissolution of the glass at the crack tip as bioactive glasses are somewhat soluble in the SBF;
3. HCA could grow on the crack flanks and wedge the crack open;
4. glass network may experience higher degree of chemical attack due to the active ionic species in the SBF.

The first phenomenon should cause decelerated subcritical crack growth relative to soda-lime glass, particularly in the near threshold regime. The second could cause accelerated crack growth compared to soda-lime glass in water if the bioactive glasses are more corrosion sensitive to SBF; however, if this dissolution is rapid, the crack growth could be decelerated relative to soda-lime glass due to crack tip blunting by the corrosion process. The third case is primarily an issue on unloading, but in service it could lead to higher average stresses on the crack tip and to shorter service lifetimes. If the ionic species in the SBF play a role, the fourth point suggests that there should be accelerated crack growth in the bioactive glasses at intermediate crack velocities, although blunting could prevail at lower velocities. The data suggest that the response of the bioactive glasses in SBF is similar to that of soda-lime glass tested in water; although, there is some indication that the crack growth for the 45S5 glass, which is more rapidly bioactive, is somewhat faster at intermediate velocities, and it may exhibit a more pronounced threshold-like behavior. Such

differences, however, remain to be verified, and it can be assumed that the typical mechanisms of SCCG in traditional silicate glasses [12] are applicable to this class of glasses as well.

4. SUMMARY

The bioactive glass 6P57 can be successfully applied to Ti–6Al–4V alloys when the temperature and time of firing are well controlled. A processing map has been developed that bounds the necessary conditions. The interface of the 6P57/Ti-alloy bond appears to be relatively tough, and the crack prefers to deflect away from the interface and extend into the glass coating under indentation loading conditions. The SCCG behavior of 6P57 has been characterized, and it appears the effect, if any, of bioactivity on subcritical crack growth is small. In fact, soda-lime–silicate glass, Bioglass[®] (45S5), and 6P57 all have similar SCCG behavior over the velocity range tested.

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REFERENCES

1. Hench, L. L., *J. Am. Ceram. Soc.*, 1998, **81**(7), 1705.
2. Krajewski, A., Ravaglioli, A., De Portu, G. and Visani, R., *Am. Ceram. Bull.*, 1985, **64**(5), 679.
3. Hench, L. L., Splinter, R. J., Allen, W. C. and Greenlee, T. K., *J. Biomed. Res. Symp.*, 1971, **2**(1), 117.
4. Pazo, A., Saiz, E. and Tomsia, A. P., *Acta mater.*, 1998, **46**(7), 2551.
5. Gamble, J., *Chemical Anatomy, Physiology, and Pathology of Extracellular Fluid*. Harvard University Press, Cambridge, MA, 1967.
6. Gomez-Vega, J. M., Saiz, E. and Tomsia, A. P., *J. Biomed. Mater. Res.*, 1999, **46**(4), 549.
7. Oku, T., Wallenberg, L., Suganuma, K., Tomsia, A. P. and Saiz, E., *J. Mat. Sci. Mat. Med.*, submitted.
8. Oku, T., Wallenberg, L. R., Suganuma, K., Tomsia, A. P. and Saiz, E., *International Symposium on Solid Junctions*, Tokyo, Japan, in press.
9. Charles, R. J., in *Progress in Ceramic Science*, ed. J. E. Burke. Pergamon Press, New York, 1961, p. 1.
10. Hillig, W. B., in *Modern Aspects of the Vitreous State*, ed. J. D. MacKenzie. Butterworth, Washington, DC, 1962, p. 152.
11. Wiederhorn, S. M., *J. Am. Ceram. Soc.*, 1967, **50**(8), 407.
12. Michalske, T. A. and Freiman, S. W., *J. Am. Ceram. Soc.*, 1983, **66**(4), 284.
13. Barry, C. and Nicholson, P. S., *Adv. Ceram. Mater.*, 1988, **3**(2), 127.
14. Wiederhorn, S. M. and Bolz, L. H., *J. Am. Ceram. Soc.*, 1970, **53**(10), 543.
15. Wiederhorn, S. M., Freiman, S. W., Fuller, E. R. and Simmons, C. J., *J. Mater. Sci.*, 1982, **17**, 3460.